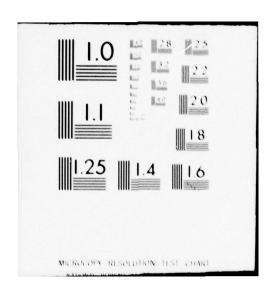
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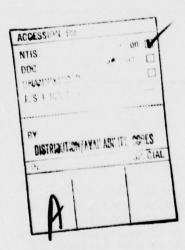
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Measurements of water vapor continuum absorption in the 3.5- to 4.0-micrometer region are presented. A deuterium fluoride grating tunable laser was used in conjunction with a 21-m long-path absorption cell. Measurements were performed at 25°C with 14.3 torr of deuterium depleted water vapor (one-fiftieth the normal concentration of HDO) buffered by pressures of 0, 250, 500, 750, 1000, and 1250 torr of an 80/20 mixture of N2/01. From the measurements of the water vapor continuum absorption

QO. / ABSTRACT (cont)

at 26 laser lines for the six foreign broadening pressures, a foreignto-self-broadening coefficient of 0.011 with a factor of 2 uncertainty was obtained. This coefficient is an order of magnitude smaller than the value of 0.12 measured (under higher temperature and pressure conditions) by other workers. Strength values for the water vapor continuum for 14.3 torr of water vapor buffered to 760 torr total pressure by an 80/20 mixture of N2/0, at 23°C previously measured in this laboratory were further substantiated by these measurements. A new model was developed for the water vapor continuum comprised of both far wing and aggregate-water-molecule type contributions. The previous 23°C data and the new 25°C data were used to calculate the water vapor continuum absorption in the 3.5- to 4.0-micrometer spectral region as a function of relative humidity for standard atmospheric pressure and ambient temperatures. Updating the presently used data base for this spectral region with these new values will have significant impact on the accuracy of the modeling of atmospheric transmission effects for Army electro-optical systems. In particular the results of this study show that the partial pressure of water vapor, especially at low total pressures, is more important than previously anticipated.



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SUMMARY

This report contains the first ambient temperature measurements of the pressure dependence of the water vapor continuum absorption in the 3.5to 4.0-micrometer spectral region. In particular, an extensive set of measurements at 25°C has resulted in a measured value of the foreignto-self-broadening coefficient of 0.011. This value was found to be frequency dependent and is an order of magnitude smaller than the value of 0.12 measured by Burch et al. at higher temperatures. This selfcontribution to the water vapor continuum was nearly an order of magnitude larger than predicted by the Burch extrapolation scheme based on his higher temperature measurements. These results were used to formulate a new model for the water vapor continuum in the 3- to 5-micrometer window. The continuum appears to have contributions from both far wing type and aggregate-water-molecule type absorption, the latter having little or no foreign broadening dependence. Calculations are presented for the absorption due to the water vapor continuum as a function of relative humidity at ambient temperature and standard pressure using the new model based on the new 25°C data and previous measurements at 23°C. The temperature dependence of this model will soon be determined by measurements in progress at the Atmospheric Sciences Laboratory (ASL) and will be reported at a later date.

The results presented in this report will increase the accuracy of modeling results used for the performance prediction and evaluation of Army and DoD electro-optical and high energy laser systems.

PREFACE

The authors thank Robert L. Spellicy for his critical review of the manuscript.

INTRODUCTION

An accurate and detailed knowledge of atmospheric transmission in and near the infrared spectral windows is essential to the design, performance evaluation, and comparative testing of electro-optical (EO) systems [1]. Of the many contributors to gaseous absorption in the atmosphere, water vapor is the most widespread spectrally and of greatest concern for many practical applications, especially for longpath high-visibility conditions. A major stumbling block to obtaining usable modeling predictions for Army EO including high energy laser (HEL) systems is lack of an accurate data base for the water vapor continuum absorption in the 3- to 5-micrometer window. Although recent measurements by the ASL have significantly improved the strength predictions for this continuum under ambient temperature and pressure conditions [1], the parameters needed to describe temperature and pressure dependences have not been addressed. Lacking the needed data base, pressure and temperature scaling parameters measured under substantially higher temperature and pressure conditions than prevail in the normal atmosphere have been the only ones available for use in modeling the water vapor continuum absorption in the 3- to 5-micrometer window [2]. The validity of using these scaling parameters has been seriously questioned by the factor of 2 difference between predicted strengths and previous measurements performed by the ASL for 14.3 torr of water vapor air broadened to 760 torr at 23°C [1]. This questioning was the impetus for performing the extensive pressure dependence study of the water vapor continuum in the 3.5- to 4.0-micrometer spectral region at 25°C.

Laboratory measurements are contained herein which improve predictive modeling of the pressure dependence of the 3- to 5-micrometer water vapor continuum absorption at ambient temperatures (i.e., at naturally occurring temperatures between 0°C and 40°C). Long-path absorption cell measurements on deuterium depleted water vapor samples have resulted in the first measures of the self-broadening contribution as well as the foreign-to-self-broadening coefficient of the 3.5- to 4.0-micrometer water vapor continuum absorption at an ambient temperature. These data can be used to infer that the ambient temperature water vapor continuum absorption in this spectral region has contributions from two different sources. The first mechanism is due to far wing absorption and has substantial foreign gas broadening dependence. The second mechanism is less understood from the standpoint of the actual absorber but may be due to some form of aggregate-water-molecule with perhaps ionic bonding present. This second mechanism has little or no dependence upon foreign gas pressure and much stronger falloff with increasing temperature than the far wing contribution. These new measurements substantially increase the accuracy of the data base used in modeling of the effects of the atmosphere on Army and Department of Defense EO including HEL systems.

STATUS OF THE AMBIENT TEMPERATURE WATER VAPOR CONTINUUM

Throughout this report, transmittance is taken to be of the form $T = \exp(-k\ell)$, where k is an absorption coefficient expressed in km⁻¹

and ℓ is the pathlength in kilometers.

Since the water vapor continuum is a residual absorption in spectral regions between strongly absorbing bands (i.e., atmospheric windows), the absorption is relatively weak (a few percent/kilometers) yet important to the operation of many EO including HEL systems [3]. To understand what causes this absorption and hence accurately model it, extensive measurements of the pressure and temperature dependencies of the continuum must be made. The physical mechanism responsible for the water vapor continuum absorption in the infrared atmospheric windows still remains in question. Several recent measurements of the continuum in the 8- to 12-micrometer window imply, in part, the existence of an aggregate-watermolecule type of absorption (perhaps water dimers) [4,5] with strong temperature and weak foreign gas broadening dependencies. Measurements of Burch et al. [2] at elevated temperatures imply a far wing type continuum in the 3- to 5-micrometer window with weaker temperature and stronger foreign gas broadening dependencies. (However, the Burch measurements do not extrapolate well to ambient temperatures, as is evidenced by the factor of 2 difference between predictions and previous ASL measurements [1].)

A detailed discussion of the functional form of the far wing type water vapor continuum has already been given elsewhere and will not be reiterated here [1]. The absorption coefficient was given as:

$$k_c(v, T) = n_s \left[c_s(v, T) p_s + c_f(v, T) p_f \right],$$
 (1)

where n_s is the number of water vapor molecules per cm³, C_s and C_f have units cm² (atm molecule)⁻¹ and are frequency (v) and temperature (T) dependent empirical parameters which qualify, respectively, self- and foreign-broadening contributions. p_s and p_f are, respectively, self (i.e., water vapor) and foreign gas partial pressure in atmospheres. In the following discussions the pressure will be given in torr instead of atmospheres with a corresponding change in the units of $C_{\mathbf{s}}$ and $C_{\mathbf{f}}$. An important quantity needed to accurately model this absorption as a function of pressure is the ratio of the foreign-to-self-broadening coefficients C_f/C_s . In the 8- to 12-micrometer window, the ratio of C_f/C_s is measured to be at most 0.005, with a lower bound of C_f/C_s approaching zero [6], which is atypical of far wing type absorption. The elevated temperature measurements of Burch give a value of C_f/C_g of 0.12 in the 3- to 5-micrometer window which is consistent with the far wing explanation of the water vapor continuum. Increased absorption in the wings of water lines (or "super"-Lorentz line shapes) has been measured for water vapor on either side of the 3- to 5-micrometer window [7,8], lending further support to the far wing explanation for a portion of the continuum absorption observed in water vapor.

ANALYTICAL AND EXPERIMENTAL APPROACH

As a first attempt to explain the factor of 2 discrepancy between the Burch predictions for the ambient temperature water vapor continuum absorption and the ASL measurements, the pressure dependence of the absorption needs to be investigated. This investigation entails measuring the self-broadening contribution C as well as the foreign-to-selfbroadening ratio C_f/C_s at ambient temperatures. For the present measurements, midlatitude summer (MLS) type conditions were used: 14.3 torr of water vapor at 25°C with varying partial pressures of air (80/20 mixture of N_2/O_2). If the Burch elevated temperature value for C_f/C_s of 0.12 is correct, then the self-term nsCsPs (no foreign broadening) would contribute about one-seventh of the total (self- and foreign-broadened) absorption at standard pressure (760 torr), while the total absorption would be increased by 50 percent if the total pressure is air broadened to 1-2/3 atmospheres (about 1260 torr). Accordingly the measurement scheme was to measure the absorption of 14.3 torr of water vapor air broadened in 250-torr intervals from 0 to 1250 torr. From these measurements the self-contribution C as well as the foreign-to-self-broadening ratio Cf/Cg can be deduced.

The water vapor continuum absorption measurements were performed by using an experimental setup described elsewhere [1,9,10]. A line tunable 3.5- to 4.0-micrometer DF laser is used in conjunction with a 21-m long-path absorption cell with conventional White-type optics. A fully automated path differencing technique [11] was used to perform these measurements - the path difference being 1512 m. The cell was maintained at the summer time laboratory nominal temperature of 25°C.

These measurements are not easy to perform for several reasons. The absorption of air broadened water vapor at each laser line is due not only to the water vapor continuum but also to line absorptions from H20 and HDO molecules and, near 4.0 micrometers, substantial absorption arises from the nitrogen continuum especially at the higher buffering pressures. The problem of relatively strong HDO line absorption is somewhat alleviated by using (as in previous experiments) [1,12] a deuterium depleted water sample with one-fiftieth the normal HDO concentration. Even with deuterium depleted water, predictions must be obtained for the line absorptions at each laser line for each buffering pressure and subtracted from the total absorption to obtain the continuum contribution. These calculations are performed by using the AFGL line parameter compilation [13], and details of the procedures are given elsewhere [1]. The problem of the nitrogen continuum absorption was essentially eliminated through the usual procedure of ratioing the transmission through an atmosphere with the deuterium depleted water vapor present to an atmosphere without the water vapor. One salient feature remained, however, in that the weak laser signals at the ends of a series, in particular the $\nu_3 \rightarrow \nu_2$ laser line series near 4.0

micrometers, were substantially attenuated by the nitrogen absorption resulting in more data scatter.

A second and even more complicating factor is the magnitude of the water vapor continuum between 3.5 and 4.0 micrometers. The relatively weak continuum absorption does not have spectral fine structure; hence, high resolution and spectral scanning are not required, but high-sensitivity absorption measurements are. The measurement of ambient temperature water vapor continuum cannot be simplified by significantly increasing the water vapor content (and hence the magnitude of the weak absorption) because condensation will result. This condensation must be strictly avoided to perform accurate long-path absorption cell measurements. Bearing in mind these factors, the measurements performed during this study were difficult to obtain even with the sophisticated long-path absorption cell used. Without the automated path differencing technique used [11], it may not have been possible to perform this study at all.

DISCUSSION OF EXPERIMENTAL RESULTS

The absorbing and nonabsorbing absolute cell transmittances represented by (as discussed in ref 14) T_a [N, 1] and T_n [N, 1], respectively, were measured at 25°C for a 37-spot (i.e., N = 37) multipath in a fully automated 21-m long-path absorption cell (i.e., L = 21 m) for 26 DF laser lines ranging in frequencies from $P_{1-0}(2)$ at 2862.646 cm⁻¹ to $P_{3-2}(11)$ at 2471.243 cm⁻¹. For the absorbing case, a pressure of 14.3 torr of deuterium depleted water vapor was used and replaced by 14.3 torr of 02 for the nonabsorbing case. Six absorbing and nonabsorbing cases were investigated with foreign gas $(80/20 \text{ mixture of } N_2/0_2)$ buffer pressures varying in 250-torr intervals from 0 to 1250 torr. The cell total pressures were thus 14.3, 264.3, 514.3, 764.3, 1014.3, and 1264.3 torr. The water vapor continuum absorption coefficients for each cell pressure are fundamentally obtained by applying the Lambert-Beer expression $T = \exp(-k\Lambda \ell)$ to the absolute transmittance of the water vapor with a $\Delta \ell$ path difference using T = T_a [37,1] / T_p [37,1] and then subtracting the water line absorption predictions [1] obtained by using the AFGL tape [13].

In these measurements the nonabsorbing absolute cell transmittance T_n [37,1] was not truly nonabsorbing because of the presence of the nitrogen continuum near 4.0 micrometers. Measurements of the nitrogen continuum have already been made by Burch [2] and can be used to obtain a correction factor (') to make the T_n [37,1] values truly nonabsorbing transmittances T_n [37,1] for each cell pressure. The same factor of course must also be used on the absorbing T_a [37,1] values corresponding to each cell pressure so as not to alter the value of the absolute transmittance of the water vapor $T = T_a$ [37,1]'/ T_p [37,1]'. Before

such a correction was performed, the nitrogen continuum absorption was checked by comparing the absolute cell transmittance for a 1512-m path difference with 1250 torr of $\rm N_2$ to 1250 torr of an $\rm O_2$ -A_r mixture (a pure $\rm O_2$ atmosphere was not used) against the Burch measurements. Three laser lines were used $\rm P_{3-2}(11)$, $\rm P_{3-2}(10)$, and $\rm P_{3-2}(9)$. The results were about 10 percent below Burch but with overlapping error bounds. Hence Burch's values were used to correct the absolute cell transmittance values.

The reason for the above discussion of correcting for the nitrogen continuum absorption will now be made clear. The measured value of the water vapor transmittance T when obtained by using path differencing exhibits almost no long-term drift error commonly associated with longpath absorption cell measurements and hence is nearly time independent [14]. The values of T_a [37,1] and T_n [37,1] at each cell total pressure should also remain time independent barring a major experimental setup change. This proved to be the case during this experiment. Now, there is no a priori reason why the nitrogen continuum corrected T [37,1]' values should not change with total cell pressure. Increased cell pressure, though nonabsorbing, does spread the laser beam and has the net effect of reducing the cell output signal. Typically 5 to 10 percent signal losses were experienced by the laser line frequencies in a monotonic fashion as the nonabsorbing gas pressure was changed from 14.3 torr to 1264.3 torr. The loss experienced was not consistent from laser line to laser line (perhaps beam geometry related) but did vary essentially linearly for each line with total cell pressure. Hence, a least squares linear fit was used on all of the $T_n[37,1]$ values for the six different cell pressures to obtain more accurate values for $T_n[37,1]$ for each cell pressure. There was some indication that the Burch nitrogen continuum absorption values were slightly high since the T_n [37,1] values for laser lines near 4.0 micrometers exhibited essentially no loss with increasing cell pressure indicating that the $\mathrm{N}_2 ext{-}\mathrm{corrections}$ overcorrected and eliminated these effects. Examples with and without the nitrogen continuum present, $P_{3-2}(9)$ and $P_{1-0}(4)$, respectively, are given in the upper plots of figures 1 and 2.

Before the absorbing absolute cell transmittance values T_a [37,1] could be analyzed, they had to be corrected for nitrogen continuum absorption plus H_20 and HD0 line absorptions so as to reflect only a transmittance loss due to the water vapor continuum before ratioing them to the corresponding T_n [37,1] values. These transmittance values are denoted as T_a [37,1]". However, using the same kind of linear smoothing on the absorbing absolute cell transmittance values T_a [37,1]" as was used on the T_n [37,1] values is not strictly valid, since if equation (1) is correct, the absorption coefficient, not absolute cell transmittance, is linear with foreign broadening pressure. Fortunately,

since the absorption coefficients are small (a few percent/kilometer), the absolute transmittance values are very nearly equal to 1 minus the absorption coefficient so that a linear fit could be applied to the absorbing absolute cell transmittance values T_a [37,1]" as well, to increase the accuracy of the values at each cell pressure (see middle plots of figures 1 and 2).

Taking the ratio of the linear curve fit values of T_2 [37,1]" to T_p [37,1]' for a given cell pressure yields the absolute transmittance due to the water vapor continuum absorption over the 1.512-km path difference. The corresponding per kilometer absorption coefficients can then be calculated for each of the six cell pressures used by dividing -ln[T] by the path difference of 1.512 km. A linear fit with respect to foreign broadening pressure was again applied to these values for each laser line to obtain more accurate values (see lower solid line plots of figures 1 and 2). The elaborate scheme of data reduction is designed to obtain the best possible values for the weak self-contribution to the water vapor continuum absorption and hence an accurate foreign-to-selfbroadening coefficient. The absorption coefficients for all 26 laser lines are listed in table 1 and are plotted in figures 3 and 8 for each cell pressure used and are compared to the Burch extrapolations (solid curves). The self-contribution shown in figure 3 is weak (a few percent/ kilometer) but not nearly as weak as the extrapolated values obtained from the elevated temperature data of Burch. In fact, the absorption is strong in comparison. Also, note that the factor of 2 difference observed previously at 23°C [1] was still present in the 25°C data at 764.3 torr total pressure. A comparison between the present work at 25°C and the previous measurement of the water vapor continuum absorption at 23°C is shown in figure 9. The present data are in general about 15 percent lower but well within the measurement uncertainty of about 0.01 km-1. Finally, comparison of the 14.3 torr data and 1264.3 torr data indicates much weaker dependence of the water vapor continuum on foreign broadening pressure than Burch measured at 155°C.

Before the actual value of the foreign-to-self-broadening is obtained, further data reduction is necessary. At each foreign broadening pressure a quadratic least squares fit of the absorption coefficient versus frequency was performed by using the data at all 26 laser frequencies. These fits are represented by the dashed lines in figures 3 to 8 and all have very similar shapes, including minimums near the same frequency. The values at each laser frequency are listed in parentheses in table 1 and shown as a dashed line linear fit for laser lines $P_{1-0}(4)$ and $P_{3-2}(9)$, respectively, in the lower plots of figures 1 and 2. An iterative process could have been used to make the curves at each pressure have exactly the same shape by performing a linear least squares fit to the quadratic curve fit values at each laser frequency for the six foreign broadening pressures.

These values could then be used to obtain a new quadratic fit of absorption versus frequency for the six foreign broadening pressures, and the process repeated. This process was not pursued because the first iteration produced only minimal changes from the curve fits shown in figures 3 to 8. Note that the quadratic fits used on the data were not perfect shape representations of the continuum absorption. The ends of the curves appear to rise too rapidly especially at the higher broadening pressures. As a result, extrapolation outside the 3.5- to 4.0-micrometer region will yield only approximate values for the water vapor continuum absorption.

The foreign-to-self-broadening coefficient B* can now be calculated for each laser frequency, but first it should be better defined. Using B* = $C_{\rm f}/C_{\rm g}$, equation (1) can be rewritten for a given laser line at 25°C and 14.3 torr of water vapor as

$$k_c(p_f) = n_g C_g (14.3 + B + p_f).$$
 (2)

Since the curve fit values of $k_c(p_f)$ vary linearly with foreign broadening pressure (see bottom dashed line plots in figures 1 and 2), only values of $k_c(0)$ and $k_c(1250)$ need be used to obtain the values of B*. The resulting expression for B* is

$$B^* = \frac{k_c(1250) - k_c(0)}{k_c(0)} \left(\frac{14.3}{1250}\right) = 0.01144 \frac{k_c(1250) - k_c(0)}{k_c(0)}$$
(3)

Values for the foreign-to-self-broadening coefficients are given in table 2 and figure 10 for all 26 laser lines. Column 2 represents B* values obtained by using the absorption coefficients after the quadratic curve fit was applied to the sets of data at $p_f=0$ and 1250 torr. There is something peculiar about these B* values of foreign-to-self-broadening which cannot be explained even when the 0.01 km $^{-1}$ measurement uncertainty of the absorption coefficients is taken into account. From figure 10, B* appears to be frequency dependent, showing smaller values near 2800 cm $^{-1}$ than at 2600 cm $^{-1}$. Column 3 represents values of B* before curve fitting, the average value for the first being 0.018 and the second 0.010. There is a problem with taking a simple average because the values of B* at laser lines where $k_{\rm c}(0)$ is small have large uncertainties due to the $1/k_{\rm c}(0)$ dependence of B*. Hence a weighted average would be more appropriate, or

$$\bar{B}^* = \frac{\sum_{i=1}^{26} B_i^* k_c(0)_i}{\sum_{i=1}^{26} - k_c(0)_i}$$
(4)

where the index represents the ith laser line. The B* values for both sets of B* values in columns 2 and 3 of table 2 gave the same weighted average value of 0.011 which is an order of magnitude smaller than the elevated temperature Burch value of 0.12.

One can conclude that the 3.5- to 4.0-micrometer water vapor continuum exhibits similar behavior to the 8- to 12-micrometer region where the continuum is thought to be due to aggregate-water-molecule absorption. One should not jump to the conclusion that there is no far wing type absorption however. Note that 65°C foreign gas broadened water vapor continuum absorption data measured at ASL supports the 0.12 value of foreign-to-self-broadening ratio rather than the 0.011 measured here at 25°C.

AMBIENT TEMPERATURE CONTINUUM MODELING

One could stop the discussion at this point and allow the readers to model for themselves the measured values of self-contribution to the water vapor continuum and the foreign-to-self-broadening ratio at ambient temperature. A method will, however, be conjectured herein which should be taken as preliminary since, though it is consistent with the results obtained thus far, it requires verification by the extensive temperature dependent study of the water vapor continuum absorption between 25°C and 65°C now being pursued at the ASL. The reason for presenting the method of course is that the authors feel that it will yield more accurate predictions than any of the presently existing models.

First the authors feel that the water vapor continuum has at least three significant terms instead of the two shown in equation (1). There should be an additional term representing a possible aggregate-water-molecule absorption (perhaps with ionic bonding) [15] of the form $n_s C_{sp}^{A} p_s$ which results in a new expression for k_c (ν , T) of

$$k_{c}(v, T) = n_{s} \left[c_{s}^{W}(v, T) p_{s} + c_{f}^{W}(v, T) p_{f} + c_{s}^{A}(v, T) p_{s} \right]$$
 (5)

where the superscripts W and A represent, respectively, far wing and aggregate contribution to the continuum absorption. The temperature dependence (as discussed later) will not be the same for the different terms. The justification for the expression is obtained by observing the behavior of the term C_8^A (v, T). If the aggregate absorption in the 3.5- to 4.0-micrometer region is similar to that in the 8- to 12-micrometer window, there will be little if any change in the absorption with foreign broadening pressure [6]. The $n_8 C_8^A$ (v, T) p_8 term gives this behavior as well as a squared dependence on the self-pressure since $n_8 \sim p_8$.

Values of $n_s C_s^A$ (v, T) p_s can be obtained for each laser line and foreign broadening pressure used by assuming that the Burch extrapolation is valid and represents only far wing type absorption which can be subtracted from the measured continuum absorption coefficients. A set of the Burch predictions for the far wing continuum contribution $n_s C_s^W$ ($p_s + 0.12 p_f$) for 14.3 torr water vapor at 25°C buffered by the various foreign broadening pressures used is given in table 3 for all 26 laser lines. The residual absorption taken as the value of ngCaps was obtained by subtracting the Burch values in table 3 from the corresponding curve fit values of total water vapor continuum absorption given in parentheses in table 1. The resulting set of neckpe values is given in table 4. At each laser line the aggregate-watermolecule absorption contribution $n_s C_s^A p_s$ is nearly independent of foreign broadening pressure within the experimental uncertainty of the measured absorption coefficients and the Burch predictions. This pressure independence is only borderline near 3.5 micrometers. However, this is the region where the ASL 65°C data did not conclusively support the Burch extrapolations. Even so it is still reasonable until a better data base is available to use the average of the six residual absorption values at each laser frequency listed in column 7 of table 4 as the value of ngCaps at 25°C.

At this point the temperature dependence of the water vapor continuum will be discussed briefly. The two far wing type terms (superscript W) in equation (5) are modeled by using the Burch temperature dependence which has the form

$$\frac{T_o}{T} = \exp\left[-m\left(\frac{1}{T_o} - \frac{1}{T}\right)\right]$$

where the $^{\rm T}_{\rm o}/^{\rm T}$ part is from the $\rm n_s$ term, the exponential is due to $\rm c_s^W$ and $\rm c_f^W$, and the coefficient m is found to be frequency dependent [16]. The $\rm c_s^A$ temperature dependence in the third term of equation (5) is not known at this time but should cause the aggregate absorption to become small at 65°C. The absorption should be far wing type dominated at 65°C since the absorption is dominated by the foreign pressure broadened term $\rm n_s \rm C_f^W p_f$ in equation (5) as evidenced by the agreement of the Burch predictions and the ASL foreign broadened measurements at 65°C. The question of how much aggregate absorption is present at 65°C is still not clear at this point.

Comparison of the previous ASL 23°C water continuum measurement with the present one is beneficial. In table 5 the Burch water vapor continuum measurement extrapolations for 14.3 torr water vapor buffered to 760 torr total pressure at 23°C (column 3) are subtracted from the ASL measurement curve fit values (column 2) to obtain the aggregate-water-molecule absorption at 23°C (column 4). The 23°C values are

within the measurement error of the 25°C aggregate-water-molecule absorption values (column 5) obtained in this study; consequently, no meaningful temperature dependence can be derived from these sets of measurements. It is at least pleasing that the 25°C values are in general smaller than the 23°C, thus hinting at a falloff of the absorption with increasing temperature as expected. What can be done is to average the two sets of values to arrive at values of $n_{\rm S} C_{\rm S}^{\rm A} p_{\rm S}$ to be used for temperatures around 24°C as in column 6 of table 5. The total continuum absorption (column 8) is obtained by adding the Burch predictions (column 7) to column 6.

In review, the proposed model for the ambient temperature has several new features. First, the water vapor continuum absorption in the 3- to 5micrometer window is assumed not to be solely due to self- and foreignbroadened far wing absorption but has an additional contribution due to a proposed aggregate-water-molecule type absorption expressed as $n_s C_s^A p_s$ with essentially no foreign broadening dependence. Second, values for this aggregate contribution can be obtained by assuming the Burch extrapolation of the far wing contribution to the water continuum based on higher temperature and pressure measurements to be valid at ambient temperatures. The Burch extrapolated values can then be subtracted from the total measured continuum absorption to give values for n_sC_sA_s. Third, the aggregate contribution must decrease more rapidly than the far wing contribution between 25°C and 65°C since the water vapor continuum is far wing dominated at 65°C. The exact expression for this dependence cannot be adequately defined until further measurements are performed. Last, bearing in mind the above, representative values of nscaps are obtained by averaging available 23°C and 25°C data to obtain estimates for the aggregate contribution around 24°C. Values for the water vapor continuum absorption can be obtained for temperatures around 24°C by adding the Burch far wing absorption for this temperature to the 24°C value of ngCApg.

The most significant departure of this new modeling scheme for the water vapor continuum at ambient temperatures will now be discussed. The water vapor continuum will not vary as expected with changes in the partial pressure of water at 760 torr total pressure atmospheres. The 24°C values of $n_{\text{S}}\text{C}_{\text{SP}_{\text{S}}}^{\Lambda}$ column 6 of table 5 and the Burch predictions are used to model equation (5) for relative humidities ranging from 10 to 100 percent in table 6 for 760 torr total pressure at 24°C . The predicted absorption values are more strongly dependent on water vapor partial pressure than previously thought because of the reduced dependence of the water vapor continuum absorption on foreign pressure broadening. Also, the absorption will not fall off as rapidly with decreasing buffer pressure as was expected with increasing altitude. Unfortunately, modeling of the water vapor continuum absorption as a function of altitude is not practical at this time because of the wide fluctuation of temperature with changes in altitude.

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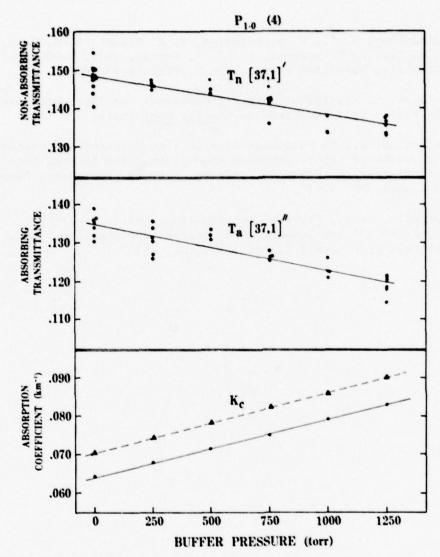


Figure 1. Cell transmittances (for a 1.512 km path difference) and corresponding water vapor continuum absorption coefficients at 25°C for DF laser line $P_{1-0}(4)$ at $2816.380~\text{cm}^{-1}$. Upper plot: Absolute nonabsorbing cell transmittance data taken for 14.3 torr of 02 buffered by 0,250,500,750,1000, and 1250 torr of air $(80/20 \text{ mixture of } N_2/0_2)$. Side-by-side data represent multiple values at same buffer pressure. No No continuum correction needed. Solid line represents linear least squares fit to data. Middle plot: Absolute absorbing cell transmittance data taken under same buffering conditions as above except 14.3 torr of deuterium depleted water vapor replaces the 14.3 torr of O2. Data are corrected for H2O and HDO line absorptions. Solid line represents linear least squares fit to data. Lower plots: Per km absorption coefficients for water vapor continuum obtained from transmittance data for each of the six buffering pressures. Circles represent absorption coefficients derived from the linear fits shown in the upper and middle plots. Solid curve is a linear least squares fit to the values thus obtained. Triangles represent absorption coefficients obtained from a least squares quadratic fit in frequency for 26 DF laser lines using the linear fit absorption coefficient (as above) at each of the six buffer pressures. Dashed line is a linear least squares fit to these values.

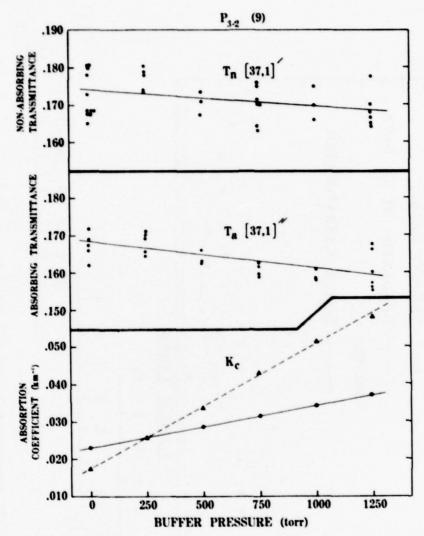
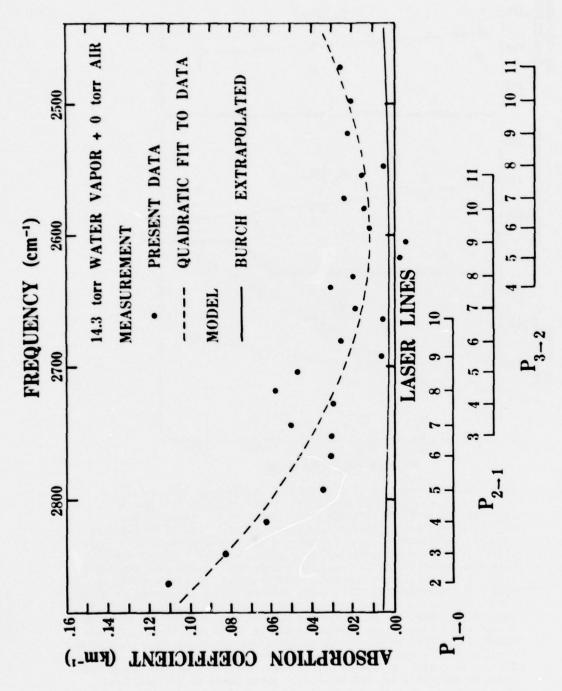
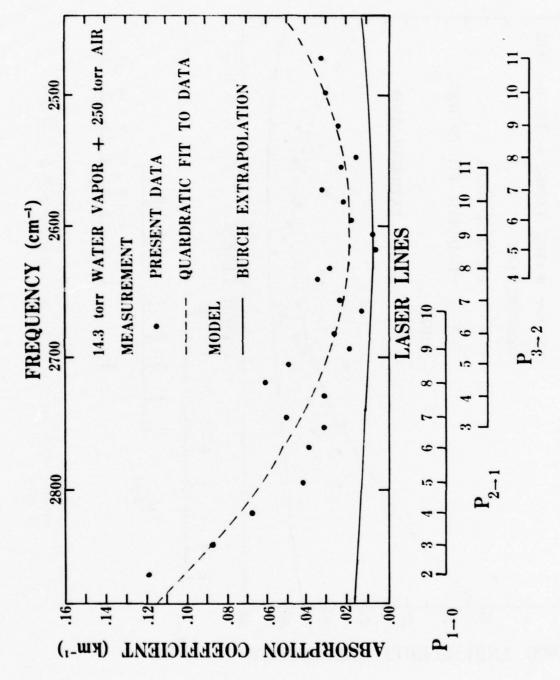


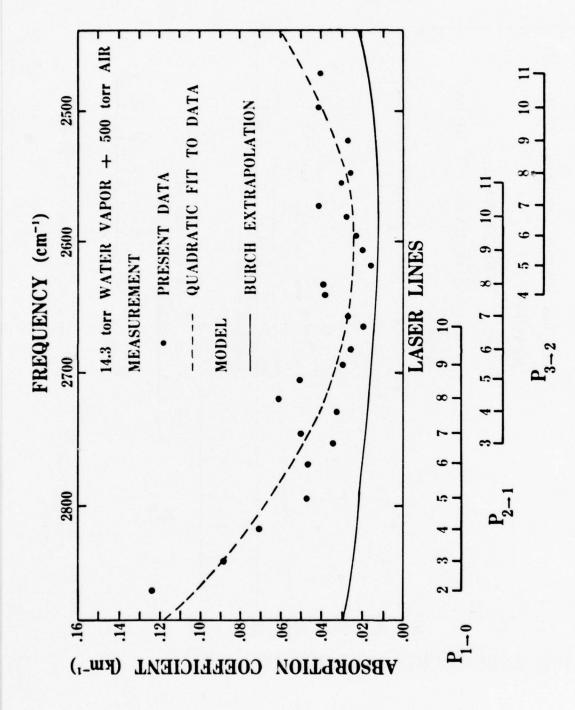
Figure 2. Cell transmittance (for a 1.512-km path difference) and corresponding water vapor continuum absorption coefficients at 25°C for DF laser line P3-2(9) at 2521.769 cm-1. Upper plot: Absolute nonabsorbing cell transmittance data taken for 14.3 torr of 02 buffered by 0,250,500,750,1000, and 1250 torr of air $(80/20 \text{ mixture of } N_2/0_2)$. Side-by-side data represent multiple values at same buffer pressure. Data are corrected for N_2 continuum absorption. Solid line represents linear least squares fit to data. Middle plot: Absolute absorbing cell transmittance data taken under same buffering conditions as above except 14.3 torr of deuterium depleted water vapor replaces the 14.3 torr of O2. Data are corrected for N2 continuum and H2O and HDO line absorptions. Solid line represents linear least squares fit to data. Lower plots: Per km absorption coefficients for water vapor continuum obtained from transmittance data for each of the six buffering pressures. Circles represent absorption coefficients derived from the linear fits shown in the upper and middle plots. Solid curve is a linear least squares fit to the values thus obtained. Triangles represent absorption coefficients obtained from a least squares quadratic fit in frequency for 26 DF laser lines using the linear fit absorption coefficient (as above) at each of the six buffer pressures. Dashed line is a linear least squares fit to these values.



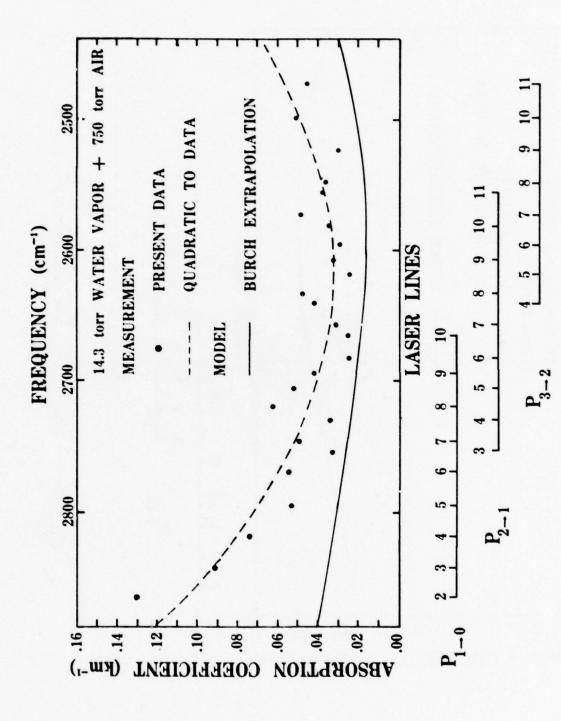
Comparison of measured water vapor continuum at $25\,^{\circ}\text{C}$ to Burch extrapolation for 14.3 torr water vapor with no air broadening. Figure 3.



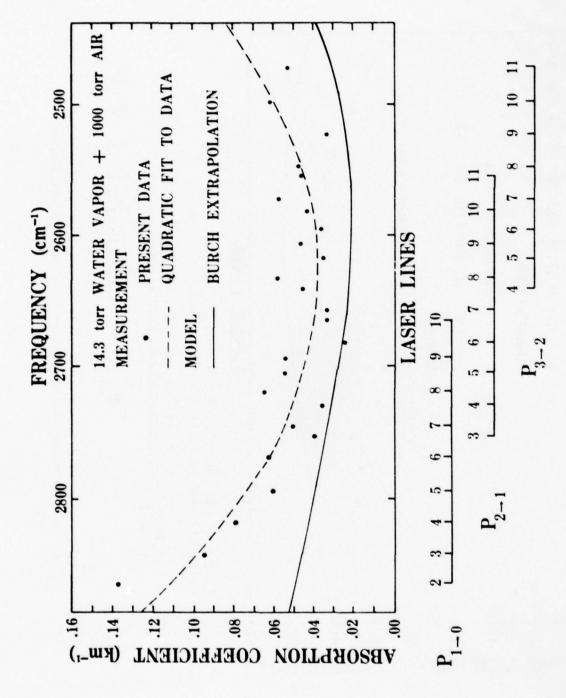
Comparison of measured water vapor continuum at 25°C to Burch extrapolation for 14.3 torr water vapor buffered by 250 torr of air. Figure 4.



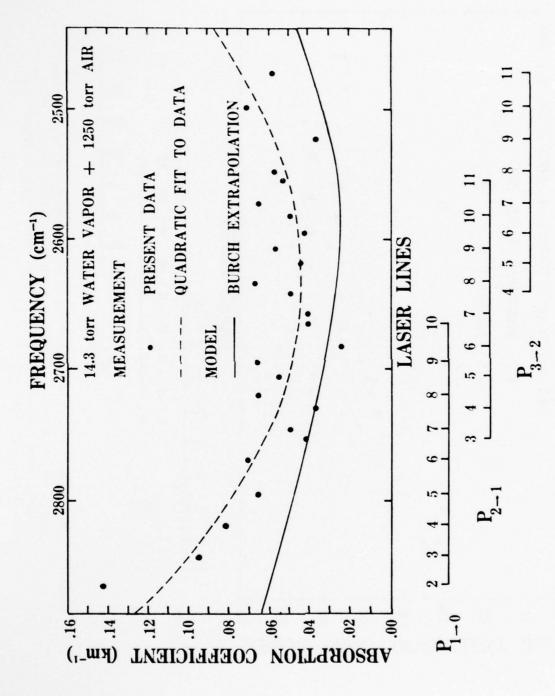
Comparison of measured water vapor continuum at $25\,^{\circ}\text{C}$ to Burch extrapolation for 14.3 torr water vapor buffered by 500 torr of air. Figure 5.



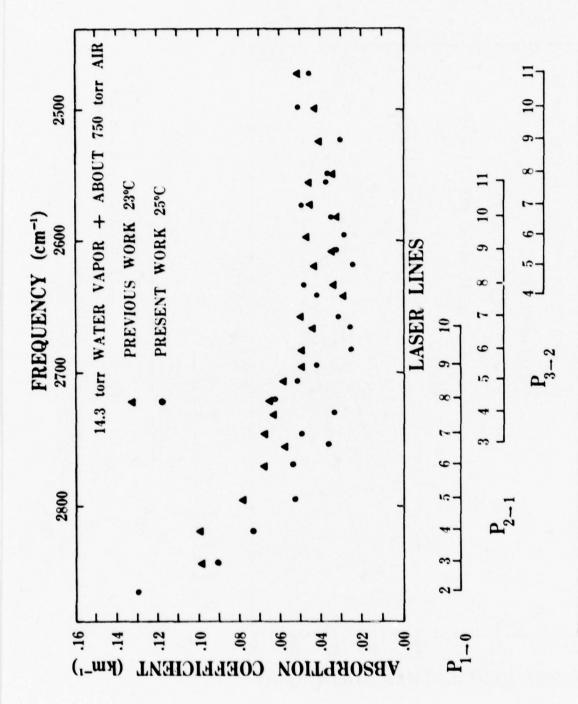
Comparison of measured water vapor continuum at 25°C to Burch extrapolation for 14.3 torr water vapor buffered by 750 torr Figure 6.



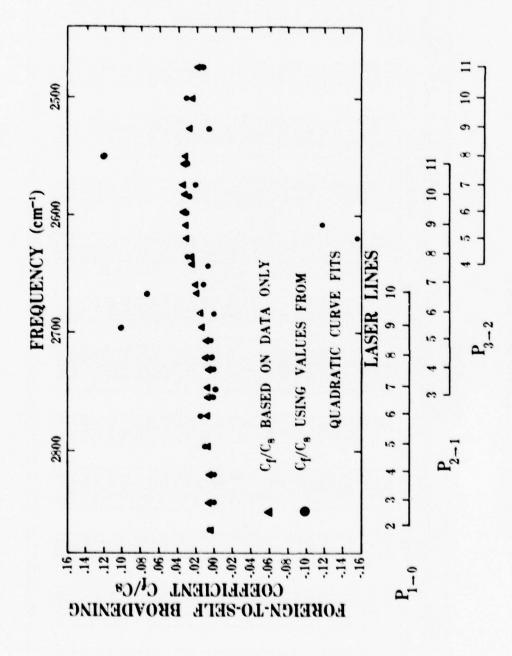
Comparison of measured water vapor continuum at 25°C to Burch extrapolation for 14.3 torr water vapor buffered by 1000 torr Figure 7.



Comparison of measured water vapor continuum at 25°C to Burch extrapolation for 14.3 torr water vapor buffered by 1250 torr Figure 8.



Comparison of previous water vapor continuum absorption measurements for 14.3 torr water vapor buffered to 760 torr at $23^\circ \rm C$ to present measurements for 14.3 torr of water vapor buffered to 764.3 torr at 25°C . Figure 9.



for the water vapor continuum at 26 DF laser lines before (circles) and after (triangles) curve fitting the measured absorption coef-Comparison of the foreign-to-self-broadening coefficients $(C_{\mathbf{f}}/C_{\mathbf{g}})$ ficients, Figure 10.

TABLE 1. MATER VAPOR ABSORPTION COEFFICIENTS (km⁻¹) FOR 14.3 TORR WATER VAPOR AT 25°C FOR SIX AIR BUFFER PRESSURES

T	7				_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_		_	_		
	-	curve Fit	(.1148	(.1017	0060.)	(.0791	(.0694	(.0634	(.0613	(.0571	(.0547)	(.0517	(.0495	(.0477	(.0460	(.0452	(.0443	(.0441	(.0442	(.0446	(.0454	(.0468	(,0480	(.0507	(.0521	(.0579	(.0653	(.0747
	1250 Torr	Measured	.1458	.0962	.0839	.0667	7170.	.0417	.0504	.0376	.0667	.0562	.0670	.0248	.0406	.0409	9640.	.0683	.0444	.0593	.0429	.0502	.0661	.0536	.0581	.0370	.0721	10591
-	Torr	Curve Fit Me	(11119)	(.0983)	(19801)	(.0749)	(.0648)	(.0585)	(.0563)	(.0519)	(.0494)	(.0462)	(.0439)	(.0420)	(.0402)	(.0393)	(.0383)	(.0381)	(.0381)	(.0385)	(.0392)	(.0406)	(.0417)	(.0445)	(.0458)	(.0516)	(.0591)	(9890)
	1000	Measured	.1391	.0040	.0792	.0604	.0635	.0395	.0505	.0362	.0653	.0546	.0549	.0253	.0336	.0336	.0459	.0586	.0349	.0462	.0366	.0430	.0579	.0460	.0474	.0342	.0618	.0527
	Torr	curve Fit	(.1072)	(.0942)	(.0824)	(.0715)	(.0616)	(.0553)	(.0531)	(.0488)	(.0461)	(.0429)	(.0405)	(.0384)	(.0363)	(.0352)	(.0339)	(.0334)	(.0331)	(.0331)	(.0335)	(.0343)	(.0351)	(.0371)	(.0382)	(.0428)	(.0489)	(.0569)
1	750	Measured	.1324	7160.	.0754	.0541	.0554	.0373	.0505	.0348	.0639	.0529	.0428	.0258	.0265	.0322	.0422	.0490	.0253	.0331	.0303	.0359	.0497	.0384	.0368	.0313	.0515	.0463
BUFFER PRESSURE	Torr	Curve Fit	(.1041)	(9060')	(.0783)	(6990)	(.0564)	(.0498)	(.0475)	(.0428)	(.0400)	(.0365)	(.0339)	(.0316)	(.0292)	(.0280)	(.0264)	(.0258)	(.0252)	(.0250)	(.0252)	(.0259)	(.0265)	(.0283)	(.0293)	(.0336)	(.0394)	(.0470)
AIR BUFFE	200	Measured	.1257	.0895	9170.	.0478	.0473	.0351	9050.	.0333	.0624	.0513	.0307	.0263	.0195	.0279	.0385	.0393	.0158	.0200	.0240	.0287	.0414	.0308	.0261	.0285	.0412	0399
	Torr	Curve Fit	.1006)	.0869)	.0774)	.0628)	.0521)	.0453)	.0429)	.0380)	.0351)	.0314)	.0286)	.0262)	.0236)	.0223)	.0204)	(9610.	.0189)	(.0185)	.0185)	.0189)	.0194)	.0208)	.0216)	.0254)	.0307)	.0378)
	250 1	Measured	.1190	.0873	.0678	.0415	.0392	.0329	0506	.0319	.0610	.0496	.0186	.0267	.0125	.0236	.0348	.0297	.0062	. no69	.0176	.0216	.0332	.0231	.0154	.0256	.0309	.0335
	Torr	Curve Fit	(0260)	(.0832)	.0705)	(.0587)	(.0477)	.0408)	(.0383)	(3333)	(.0302)	(.0263)	(.0234)	(.0208)	(8710.)	(.0165)	(,0144)	(.0135)	(.0125)	(.0120)	(7110.)	(6110.)	(.0122)	(.0134)	(.0140)	(.0173)	(.0221)	(.0286)
	0 10	Measured	.1123	.0850	.0640	.0353	0310	.0307	.0507	.0305	9650.	.0479	.0065	.0272	.0054	.0192	.0311	.0200	0034	0062	.0113	.0144	.0250	.0155	.0048	.0228	.0206	.0271
Wavenumber	(cm-1)		2862.646	2839.791	2816.380	2792.434	2767.968	2750.093	2742.997	2727.308	2717.538	2703.998	2691.608	2680.178	2665.218	2655.863	2640.075	2631.066	2617.386	2605.806	2594.197	2580.095	2570.522	2553.951	2546.373	2521.769	2496.720	2471.243
Laser	Line		(2)	(3)	P, (4)	(2)	(9)	2(3)	(7)	2(4)	1(8)	(2)	1(6)	(9)	1(10)	2(7)	3(4)	(8)	(2)	6	P ₃ (6)	(10)	(7)	(11)	(8)	(6)	P3(10)	(11)

TABLE 2. FOREIGN-TO-SELF BROADENING COEFFICIENTS (C $_{f}/\text{C}_{s}$) FOR 14.3 TORR WATER VAPOR CONTINUUM AT 25°C

Laser Line	Foreign-	to-self Broadening Co	pefficients
	fr		
	Curve Fit	Measurements	
D (2)	0001	0004	
P ₁ (2)	.0021	.0034	
Pi (3)	.0025	.0015	
Pi(4)	.0032	.0034	
P1(5)	.0040	.0102	
P1(6)	.0052	.0150	
P2(3)	.0063	.0041	
P ₁ (7)	.0069	0001	
P2(4)	.0082	.0026	
P ₁ (8)	.0093	.0014	
P ₂ (5)	.0110	.0020	
$P_{1}(9)$.0128	.1065	
P ₂ (6)	.0149	0010	
P ₁ (10)	.0181	.0746	
$P_{2}(7)$.0199	.0129	
$P_{2}^{2}(4)$.0238	.0068	
P ₂ (8)	.0259	.0276	
P ₃ (5)	.0290	1608	
P ₂ (9)	.0311	1209	
P ₃ (6) P ₂ (10)	.0330	.0320	
P ₂ (10)	.0336	.0284	
P ₃ (7)	.0336	.0188	
P ₂ (11)	.0318	.0281	
Pa(8)	.0311	.1270	
P ₃ (8) P ₃ (9) P ₃ (10)	.0268	.0071	
P3(10)	.0224	.0286	
P3(11)	.0184	.0135	
13(11)	.0104	.0133	

TABLE 3.

BURCH EXTRAPOLATIONS FOR THE WATER VAPOR CONTINUUM ABSORPTION FOR 14.3 TORR WATER VAPOR AT 25°C FOR VARIOUS AIR BROADENING PRESSURES

Burch Extrapolated Absorption Coefficients (km⁻¹) For Different Air Broadening Pressures Laser Line 0 Torr | 250 Torr 500 Torr 1750 Torr 1000 Torr 1250 Torr P1(2) P1(3) P1(4) P1(5) P1(6) P2(3) P1(7) P2(4) P1(8) .0052 .0161 .0271 .0380 .0489 .0599 .0049 .0152 .0255 .0358 .0461 .0564 .0046 .0142 .0239 .0335 .0431 .0528 .0043 .0132 .0222 .0311 .0401 .0491 .0039 .0122 .0205 .0287 .0370 .0453 .0037 .0115 .0192 .0270 .0348 .0425 .0036 .0112 .0187 .0263 .0339 .0414 .0034 .0105 .0176 .0248 .0319 .0390 .0101 .0170 .0033 .0238 .0306 .0375 P2(5) .0031 .0095 .0160 .0225 .0289 .0354 P₁(9) P₂(6) .0029 .0091 .0153 .0214 .0276 .0337 .0028 .0087 .0147 .0206 .0265 .0324 P1(10) .0027 .0083 .0139 .0195 .0251 .0303 P2(4) P2(4) P2(8) P3(5) P3(6) P2(6) P2(7) P3(11) P3(8) P3(10) P3(11) .0025 .0080 .0135 .0189 .0244 .0298 .0025 .0076 .0128 .0180 .0231 .0283 .0024 .0074 .0124 .0175 .0225 .0275 .0023 .0071 .0119 .0167 .0216 .0264 .0022 .0069 .0162 .0115 .0209 .0255 .0022 .0205 .0068 .0114 .0160 .0251 .0022 .0068 .0115 .0161 .0208 .0254 .0022 .0069 .0117 .0164 .0211 .0258 .0023 .0072 .0121 .0170 .0219 .0268 .0024 .0074 .0124 .0175 .0225 .0275 .0026 .0137 .0082 .0193 .0248 .0304 .0218 .0030 .0092 .0155 .0280 .0343 .0033 .0104 .0174 .0244 .0314 .0385

ABSORPTION (km-1) FOR 14.3 TORR WATER VAPOR AT 25°C FOR VARIOUS AIR BROADENING PRESSURES TABLE 4. AGGREGATE-WATER-MOLECULE CONTRIBUTION (nsc^âps)to the water vapor continuum

Average Value of nsCsps	and Standard Deviation			-	-	.0423 ±.0091	*1	•	*1	*	1	*	*	*1	+1	*1	+1	*1	+1	+1	+1	*1	+1	+1	+1	+1	+1	+1
ion		1250 Torr	.0549	.0453	.0372	.0300	.0241	.0209	.0199	.0181	.0172	.0163	.0158	.0153	.0152	.0154	.0160	.0166	.0178	1610.	.0203	.0214	.0222	.0239	.0246	.0275	.0310	.0352
ntribut		1000 Torr	.0630	.0522	.0430	.0348	.0278	.0237	.0224	.0200	.0188	.0173	.0163	,0155	.0151	.0149	.0152	.0156	.0165	.0176	.0187	.0198	.0206	.0226	.0233	.0268	.0311	.0362
ecule Co	ened by	75U Torr	.0692	.0584	.0489	.0404	.0329	.0283	.0268	.0240	.0223	.0204	1610.	.0178	.0168	.0163	.0159	.0159	.0164	.0169	.0175	.0182	.0187	.0201	.0207	.0235	.0271	.0325
Aggregate-Water-Molecule Contribution	Air Broadened by	500 Torr	.0788	.0651	.0544	.0447	.0359	.0306	.0288	.0252	.0230	.0205	.0186	.0168	.0153	.0145	.0136	.0134	.0133	.0135	.0138	.0144	.0148	.0162	.0169	.0199	.0239	.0296
regate-W	A	250 Torr	.0845	7170.	7090	.0496	.0399	.0338	.0317	.0275	.0250	.0219	.0195	.0175	.0153	.0143	.0147	.0122	.0117	.0115	7110.	.0121	.0125	.0136	.0142	.0172	.0215	.0280
Agg		Torr	8160.	.0783	.0659	.0544	.0438	.0371	.0347	.0299	.0269	.0232	.0205	.0180	.0151	.0139	.0119	.0111	.0102	.0098	.0095	7600.	.0100	1110.	.0116	.0147	.0191	.0253
Laser	Line		P, (2)	P;(3)	P, (4)	P ₁ (5)	P ₁ (6)	P ₂ (3)	P ₁ (7)	P ₂ (4)	P ₁ (8)	P ₂ (5)	P ₁ (9)	P, (6)	P ₁ (10)	P ₂ (7)	P3(4)	P ₂ (8)	P3(5)	P2(9)	P ₃ (6)	P ₂ (10)	P3(7)	P ₂ (11)	P ₂ (8)	P3(9)	P ₂ (10)	P3(10)

TABLE 5.
CONTRIBUTIONS TO THE WATER VAPOR CONTINUUM ABSORPTION (km⁻¹) AT AMBIENT TEMPERATURES FOR 14.3 TORR WATER VAPOR

		-	1																									
ASL	Mode Le	24°C	7911.	.1031	8060.	.0794	.0688	.0621	.0598	.0549	.0519	.0482	.0455	.0429	.0403	.0389	.0372	.0352	.0354	.0349	.0349	.0351	.0356	.0370	.0377	.0413	.0464	.0530
24°C Burch	Extrapola- tions	nsCs (ps+.12ps)	,0375	.0353	.0330	.0307	.0283	.0266	.0260	.0244	.0234	.0221	.0212	.0203	.0193	.0186	.0177	.0172	.0166	.0159	.0158	.0159	.0162	6910.	.0172	0610.	.0215	.0241
Average	(24°C)	nsc _s ps	.0792	.0678	.0578	.0487	.0405	.0355	.0338	.0305	.0285	.0261	.0243	.0226	.0210	.0203	.0195	0610.	.0188	.0190	1610.	.0192	.0194	.0201	.0205	.0223	.0249	.0289
	25°C	nsugps	.0737	.0618	.0516	.0423	.0341	.0291	.0274	.0241	.0222	.0199	.0183	.0168	.0155	.0149	.0146	.0141	.0143	.0147	.0153	.0159	.0165	.0179	.0186	.0216	.0256	.0311
	23°C	sdsasu (s	.0846	.0738	.0640	.0551	.0469	.0418	.0401	.0368	.0348	.0322	.0302	.0284	.0265	.0257	.0243	.0238	.0233	.0232	.0228	.0225	.0223	.0222	.0223	.0229	.0241	.0267
23°C'Burch Extrapola-	tions nscs	(ps + .12p	.0383	.0360	.0337	.0313	.0289	.0272	.0265	.0249	.0239	.0226	.0216	.0207	7610.	.0190	.0181	.0176	.0169	.0162	.0161	.0162	.0165	.0172	.0176	.0194	.0219	.0246
•	¥ ;	values 23°C	.1229	.1098	7260.	.0864	.0758	0690	9990.	7190.	.0587	.0548	.0518	.0491	.0462	.0447	.0424	.0414	.0402	.0394	.0389	.0387	.0388	.0394	.0399	.0423	.0460	.0513
	300	Line	-	P, (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	P ₂ (8)	-	-	-	P ₂ (10)	P ₂ (7)	P ₂ (11)	P ₂ (8)	P3(9)	P3(10)	P ₃ (11)

TABLE 6.

STANDARD		100%	.2567	.2251	1968	1465	.1314	.1263	.1155	.1089	1009	0360	.0893	.0837	.0808	.0774	.0753	.0738	.0731	.0732	.0736	.0746	.0775	0620.	.0864	6960.	E .
FOR		206	.2125	1867	1634	1222	1097	.1055	9960.	1160.	.0844	.0795	.0748	.0702	8290.	.0648	.0631	.0618	.0612	.0612	9190.	.0624	.0649	1990.	.0723	.0812	.0930
IONS AT 24°C MODEL		80%	.1725	1517	1331	1000	.0899	.0865	.0793	.0748	.0694	.0654	9190.	.0578	.0558	.0534	.0520	.0509	.0503	.0503	9050.	.0513	.0533	.0543	.0595	.0667	.0764
NEW		70%	.1365	1204	1059	0799	.0720	.0693	.0636	.0601	.0553	.0526	.0496	.0466	.0450	.0430	.0418	.0409	.0404	.0404	.0406	.0412	.0428	.0435	.0478	.0537	.0614
r (km ⁻¹) PRED TORR) USING	DITY	%09	.1048	.0927	.0817	1621	.0561	.0540	.0496	.0470	.0436	.0412	.0389	.0365	.0352	.0337	.0328	.0321	.0316	.0316	.0318	.0322	.0335	.0341	.0374	.0420	.0480
(760 TOF	RELATIVE HUMIDITY	20%	1770.	.0684	.0605	0464	.0420	.0405	.0373	.0353	.0328	.0310	.0293	.0276	.0266	.0254	.0247	.0242	.0237	.0237	.0239	.0242	.0252	.0257	.0281	.0316	.0361
ON COEFFICIENT PRESSURE (760	RELAT	40%	.0534	.0477	.0424	0328	.0298	.0288	.0265	.0251	.0234	.0222	.0210	.0198	.0191	.0182	.0177	.0173	.0169	6910.	.0170	.0173	.0180	.0183	.0201	.0226	.0257
UUM ABSORPTIO ATMOSPHERIC P		30%	.0339	.0304	.0272	0213	.0195	.0189	.0174	.0165	.0154	.0147	.0139	.0131	.0126	.0121	.0117	.0114	.0112	.0111	.0112	.0114	.0118	.0121	.0133	.0149	.0169
CONTINUUM ABSORPTION ATMOSPHERIC PRE		20%				1210																					
POR		10%		9900		0000																					
WATER VA	Laser Line		P, (2)	P ₁ (3)	P. (4)	(6)	P;(3)	p ₁ (7)	P ₂ (4)	P ₁ (8)	P ₂ (5)	P ₁ (9)	P ₂ (6)	P ₁ (10)	P ₂ (7)	P ₂ (4)	P ₂ (8)	P ₂ (5)	P ₂ (9)	P ₂ (6)	P ₂ (10)	P ₂ (7)	-	P3(8)	P-(9)	P ₃ (10)	P3(11)

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